

## CMB7 Procedures for Treating Secondary PM-10 Particles

One of the key assumptions made by CMB7 is that chemical species do not react with each other (Section A.3 of the CMB7 User's Guide<sup>1</sup> and Section C.1 of the CMB Protocol<sup>2</sup>), i.e., that "compositions for the source categories are obtainable which represent the source profile as it is perceived at the receptor" for the chemical species of interest (Section 3.1 of the CMB Protocol). Thus, CMB7 assumes no changes to the aerosol during transport and ideally apportions the primary material that has not changed between source and receptor. However, certain species, e.g., sulfur (S), that dominate polluted airsheds have both primary and secondary sources.

In such airsheds (e.g., many designated "Serious PM-10 Areas" by EPA), secondary aerosols may contribute significantly to the ambient loading seen at receptors. These secondary materials are often in the form of reactive species such as  $\text{NH}_4^+$ ,  $\text{SO}_4^-$ ,  $\text{NO}_3^-$ , and organic carbon. If sources of such materials are not explicitly treated, CMB7 will tend to underaccount for total particle mass (% MASS value in the Source Contribution Display; see Section 3.3.1 of the CMB Protocol). As stated in Section 3.2.1 of the CMB Protocol, "if a compound which is secondarily formed or is normally associated with regional scale pollution (such as sulfate) is included as a fitting species, a 'single constituent source type' ... must also be included in the fit ..." Use of the *single constituent source profile* for secondary particles was initially suggested by Watson (1979)<sup>3</sup> and is described briefly in the Section 3.2.2 of the CMB Protocol. With this technique, the secondary species are "apportioned to chemical compounds rather than directly to sources" (Section A.4 of the CMB7 User's Guide).

Table 1 illustrates an example of the way the technique was used in an actual application for California's South Coast Air Basin (Watson et al., 1994<sup>4</sup>). Secondary source profiles consisting of "pure" ammonium sulfate (AMSUL), ammonium bisulfate (AMBSUL), ammonium nitrate (AMNIT), and organic carbon (OC) were used to apportion the remaining  $\text{NH}_4^+$ ,  $\text{SO}_4^-$ ,  $\text{NO}_3^-$ , and OC that would not be apportioned to the primary particle profiles. For some secondary species thought to be significant (e.g., note the OC column), a source profile was created which includes only that component, in which the percentage composition in the profile is set to 100%. For other secondary species, only some chemical components may have been measured. For instance, elemental S and/or sulfate ion ( $\text{SO}_4^-$ ) may be measured rather than ammonium sulfate,  $(\text{NH}_4)_2\text{SO}_4$ . In such a case, the respective species abundances in the  $(\text{NH}_4)_2\text{SO}_4$  would equal the mass % of each species in  $(\text{NH}_4)_2\text{SO}_4$ . Thus, in the AMSUL profile the abundance of S in pure  $(\text{NH}_4)_2\text{SO}_4$  is listed as 24.3% and the abundance of  $\text{SO}_4^-$  is listed as 72.7%. Examples are also given for other secondary species and their chemical components. In all cases, the uncertainty was arbitrarily set to 10%. In the CMB7 calculations, the portion of a measured secondary species not accounted for by other source types becomes assigned to its corresponding single constituent source type, as represented by profiles such as those described here.

The examples given above are described as profiles for secondary species. However, the secondary profile may not represent secondary aerosol exclusively. For example, Watson et al. (1994) indicate that the OC profile in Table 1 may account for contributions from fugitive sources not included in the CMB7 calculation (e.g., cooking, plant parts, or tire wear) in addition to secondary sources. In such a case, the technique may be considered as a means to get an upper estimate of the amount of aerosol attributable to secondary formation.

One of the advantages of using the single constituent source profile technique is that it can account for that part of the ambient mass that is not accounted for by the primary sources included in the CMB7 calculations. However, this technique **cannot** yield any information on the specific source types contributing to the species in the single constituent profiles. Furthermore, the ambient mass may still be underestimated in some cases. For example, Conner et al. (1993)<sup>5</sup> reported that fine particle mass may have been underaccounted for in their CMB7 calculations because of the likelihood for some amount of water associated with hygroscopic (or deliquescent) sulfates. The amount of mass due to this water depends of the form of the sulfate and relative humidity factors.

**Table 1. Secondary Aerosol Source Profiles (Weight % of Mass)**

Species <sup>b</sup>	AMSUL			AMBSUL			AMNIT			OC		
	PM <sub>2.5</sub> & Coarse <sup>c</sup>			PM <sub>2.5</sub> & Coarse <sup>c</sup>			PM <sub>2.5</sub> & Coarse <sup>c</sup>			PM <sub>2.5</sub> & Coarse <sup>c</sup>		
	Conc. ± Unc. <sup>d</sup>			Conc. ± Unc. <sup>d</sup>			Conc. ± Unc. <sup>d</sup>			Conc. ± Unc. <sup>d</sup>		
Cl <sup>-</sup>	0.000	±	0.000	0.000	±	0.000	0.000	±	0.000	0.000	±	0.00
NO <sub>3</sub> <sup>-</sup>	0.000	±	0.000	0.000	±	0.000	77.5	±	7.8	0.000	±	0.00
SO <sub>4</sub> <sup>=</sup>	72.7	±	7.3	83.5	±	8.3	0.000	±	0.000	0.000	±	0.00
NH <sub>4</sub> <sup>+</sup>	27.3	±	2.7	15.7	±	1.6	22.6	±	2.3	0.000	±	0.00
Na <sup>+</sup>	0.000	±	0.000	0.000	±	0.000	0.000	±	0.000	0.000	±	0.00
TC	0.000	±	0.000	0.000	±	0.000	0.000	±	0.000	100	±	10
OC	0.000	±	0.000	0.000	±	0.000	0.000	±	0.000	100	±	10
EC	0.000	±	0.000	0.000	±	0.000	0.000	±	0.000	0.000	±	0.00
Na	0.000	±	0.000	0.000	±	0.000	0.000	±	0.000	0.000	±	0.00
Al	0.000	±	0.000	0.000	±	0.000	0.000	±	0.000	0.000	±	0.00
Si	0.000	±	0.000	0.000	±	0.000	0.000	±	0.000	0.000	±	0.00
P	0.000	±	0.000	0.000	±	0.000	0.000	±	0.000	0.000	±	0.00
S	24.3	±	2.4	27.9	±	2.8	0.000	±	0.000	0.000	±	0.00
Cl	0.000	±	0.000	0.000	±	0.000	0.000	±	0.000	0.000	±	0.00
K	0.000	±	0.000	0.000	±	0.000	0.000	±	0.000	0.000	±	0.00
Ca	0.000	±	0.000	0.000	±	0.000	0.000	±	0.000	0.000	±	0.00
Ti	0.000	±	0.000	0.000	±	0.000	0.000	±	0.000	0.000	±	0.00
V	0.000	±	0.000	0.000	±	0.000	0.000	±	0.000	0.000	±	0.00
Cr	0.000	±	0.000	0.000	±	0.000	0.000	±	0.000	0.000	±	0.00
Mn	0.000	±	0.000	0.000	±	0.000	0.000	±	0.000	0.000	±	0.00
Fe	0.000	±	0.000	0.000	±	0.000	0.000	±	0.000	0.000	±	0.00

<sup>a</sup>Reproduced with permission from Watson et al. (1994)

<sup>b</sup>TC (Total Carbon) = OC + EC; Sum does not include Na<sup>+</sup>, Cl<sup>-</sup>, S, or TC.

<sup>c</sup>PM<sub>10</sub> - PM<sub>2.5</sub>

<sup>d</sup>Conc is the average abundance (% of total mass) for several samples of emissions from the same source type. Unc. is the standard deviation of the abundances for these samples.

Ni	0.000	±	0.000	0.000	±	0.000	0.000	±	0.000	0.000	±	0.00
Cu	0.000	±	0.000	0.000	±	0.000	0.000	±	0.000	0.000	±	0.00
Zn	0.000	±	0.000	0.000	±	0.000	0.000	±	0.000	0.000	±	0.00
As	0.000	±	0.000	0.000	±	0.000	0.000	±	0.000	0.000	±	0.00
Se	0.000	±	0.000	0.000	±	0.000	0.000	±	0.000	0.000	±	0.00
Br	0.000	±	0.000	0.000	±	0.000	0.000	±	0.000	0.000	±	0.00
Sr	0.000	±	0.000	0.000	±	0.000	0.000	±	0.000	0.000	±	0.00
Mo	0.000	±	0.000	0.000	±	0.000	0.000	±	0.000	0.000	±	0.00
Cd	0.000	±	0.000	0.000	±	0.000	0.000	±	0.000	0.000	±	0.00
Sn	0.000	±	0.000	0.000	±	0.000	0.000	±	0.000	0.000	±	0.00
Sb	0.000	±	0.000	0.000	±	0.000	0.000	±	0.000	0.000	±	0.00
Ba	0.000	±	0.000	0.000	±	0.000	0.000	±	0.000	0.000	±	0.00
Hg	0.000	±	0.000	0.000	±	0.000	0.000	±	0.000	0.000	±	0.00
Pb	0.000	±	0.000	0.000	±	0.000	0.000	±	0.000	0.000	±	0.00
Sum	100	±	8	99.1	±	8.5	100	±	8	100	±	10

#### REFERENCES

1. Environmental Protection Agency, 1990. Receptor Model Technical Series, Volume III: CMB7 User's Manual. EPA-450/4-90-004. U.S. Environmental Protection Agency, Research Triangle Park, NC.
2. Environmental Protection Agency, 1987. Protocol for Applying and Validating the CMB Model. U.S. Environmental Protection Agency, Research Triangle Park, NC.
3. Watson, J. G., 1979. Chemical Element Balance Receptor Model Methodology for Assessing the Sources of Fine and Total Suspended Particulate Matter in Portland, Oregon. Ph.D. Dissertation, Oregon Graduate Center, Beaverton, OR; pp. 412-413.
4. Watson, J.G., J.C. Chow, Z. Lu, E.M. Fujita, D.H. Lowenthal, D.R. Lawson, and L.L. Ashbaugh, 1994. Chemical Mass Balance Source Apportionment of PM<sub>10</sub> during the Southern California Air Quality Study. *Aerosol Sci. Technol.*, 21(1): 1-36.
5. Conner, T.L., J.L. Miller, R.D. Willis, R.B. Kellogg, and T.F. Dann, 1993. Source Apportionment of Fine and Coarse Particles in Southern Ontario, Canada. Presented at the 86th Annual Meeting and Exhibition, Air & Waste Management Association, Denver, CO; 13 - 18 June 1993.